III.A.22 Novel Composite Materials for SOFC Cathode-Interconnect Contact

Objectives

- Elucidation of the mechanism of Ag evaporation at elevated temperatures.
- Alloy design of new Ag-based alloys with significantly reduced Ag evaporation/migration.
- Optimization of the processing and the microstructures of Ag alloy/perovskite composites.
- Demonstration/assessment of performance of the new contact materials.

Accomplishments

- Elucidated the Ag evaporation mechanism based on the experimental evaluation of various factors affecting the evaporation rate of pure Ag.
- Identified the optimal conditions for evaluating the Ag evaporation of Ag-based alloys as contact material: exposure environment – flowing air; air flow rate – 1.5 $cm.s^{-1}$; exposure temperature – 850°C; exposure time – 40 hours.
- Synthesized a well-distributed $Ag+La_{0.8}Sr_{0.2}CoO_3$ composite with an average particle size of less than 1 µm via a glycine nitrate combustion process.

Introduction

To reduce the electrode/interconnect interfacial resistance in SOFC stacks, electrical contact layers are often applied between the interconnect and electrodes during construction of an SOFC stack by compensating for the corrugations present on their respective surfaces. Three major criteria for SOFC contact materials are (1) sufficient high electrical conductivity over the SOFC lifetime; (2) chemical stability under high current condition and compatibility with other cell components, especially negligible effects on the formation of protective oxides on interconnect alloy; and (3) reasonable match in coefficient of thermal expansion (CTE) with other cell components. Because of the stringent criteria, finding a suitable material for the interconnect-cathode contact is very challenging, particularly in the intermediate temperature (600-800°C) SOFCs where high-temperature oxidation-resistant alloys are used as interconnect material.

The materials currently under consideration for cathode/interconnect contact application include low melting-point ceramics (such as doped $LaCoO_3$), noble metals (e.g. Ag or Pt), and their composites [1-3]. Pt, Au, and Pd are not desirable for this application because of their high raw material cost. However, Ag is an exception due to its relatively low price. Ag-ceramic composite is one of the very promising candidates for SOFC contact due to the inherent properties of Ag, such as high chemical stability, high electrical conductivity, high ductility, and relatively low melting point. The perovskite component in the composite is expected to provide a more desirable CTE match and act as a Cr absorbent and/or a barrier for Cr migration to the cathode. One major drawback of Ag as SOFC interconnect/cathode contact material is its tendency to evaporate at the SOFC operating temperatures and subsequent migration to other cell components, potentially causing the cell performance degradation. To date, the evaporation behavior of Ag under SOFC operating conditions has not been systematically investigated, even though numerous studies have been carried out on thermal etching of Ag at elevated temperatures [4-6].

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Approach

Ag would be a wonderful contact material if its evaporation/migration can be reduced. Alloying with other elements such as noble metals, surface-active elements, or certain transition metals might reduce the evaporation/migration of Ag. What is desired of the alloying elements is to effectively reduce Ag evaporation/migration without significantly altering the overall properties of Ag. To provide guidelines for the selection of alloying additions, fundamental studies on the evaporation mechanism of Ag at elevated temperatures are being conducted. Based on the mechanistic understanding, alloy design and physical metallurgy principles will be employed for developing a series of new Ag-base alloys with significantly reduced Ag evaporation rates. These alloys will be evaluated under realistic SOFC operating conditions; furthermore, Ag alloy/perovskite composites will be synthesized and the performance of the composite materials as interconnect/cathode contacts will be assessed.

Results

The effects of a number of exposure parameters such as time, temperature, and air flow rate on Ag evaporation were investigated. For all evaporation experiments, a linear relationship was observed between the weight loss of Ag and the duration of thermal exposure. As illustrated in Figure 1, the weight loss of pure Ag after 50-hour exposure at both 900°C and 850°C initially increased linearly with air flow rate and then reached a plateau at a flow rate of about 1.0 cm.s^{-1}; further increase in air flow rate had no effect on the Ag evaporation, i.e. a plateau was observed. The loss of weight at the flow rate above 1.0 cm.s^{-1} was about 2.6 times of that in stagnant air for both exposures at 900°C and 850°C. It is concluded that when Ag vapor pressure is below a critical point, the evaporation rate of Ag is controlled by both evaporation from the surface of solid Ag and back-condensation of Ag vapor. Therefore, the net evaporation rate is the difference of these two processes. If the vapor pressure of Ag drops below that critical value, the evaporation of Ag is essentially controlled by the evaporation process alone.

To determine the effect of temperature on Ag evaporation rate, a relatively high air flow rate of 1.5 cm.s^{-1} was selected as a standard flow rate and the test temperature was varied from 750ºC to 925ºC. It was found that the evaporation rate of pure Ag increased significantly with exposure temperature. An exponential relation was obtained between the weight loss of Ag and the reciprocal of temperature, as shown in Figure 2. The heat of Ag evaporation, calculated from the slope of the figure, was equal to 280 KJ.mol^{-1}. The heat of evaporation was very close to the heat of atomization for pure Ag, which is 284.09 KJ.mol^{-1}. This implies that the evaporation of Ag under these conditions is essentially controlled by breaking of the bond between Ag atoms in the solid state. Several evaporation experiments were carried out in the presence of various vapor phase constituents, such as air, air+3%H_2O, Ar+5%H_2, or Ar+5%H_2+3%H_2O. The results indicate that none of the exposing atmospheres had a measurable influence on the evaporation rate of Ag, i.e. the Ag evaporation rate is essentially the same in both reducing and oxidizing atmospheres.

The surface morphological features of pure Ag after thermal exposure were also observed with a scanning electron microscope (SEM). As is clear from Figures 3(a)-(c), the samples exposed to air developed a striation structure (parallel ledges) after thermal exposure at temperatures from 750°C to 900°C. The space between the ledges increased with the increase in exposure temperature. However, very smooth surfaces only with some grain boundary grooves were observed after thermal exposure in both Ar+5%H_2 and Ar+5%H_2+3%H_2O (Figure 3(d)).

This study indicates that with typical SOFC operating conditions, such as an air flow rate of 1.1 cm.s^{-1} at 800°C in air, the evaporation rate of Ag is 4x10^{-10} g.cm^{-2}.s^{-1}. This value is very high considering the targeted SOFC operation time of 40,000 hours. Therefore, pure Ag is not suitable for this application due to its excessive evaporation during service. However, since the evaporation of Ag is determined by breaking of the bond between Ag atoms in the solids, alloying with other elements that increase the bonding energy might

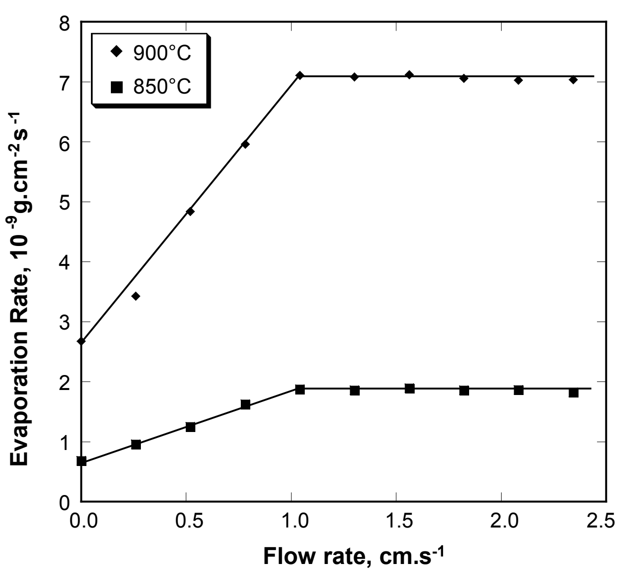

FIGURE 1. The Evaporation Rate of Pure Ag as a Function of Air Flow Rate at Both 900°C and 850°C

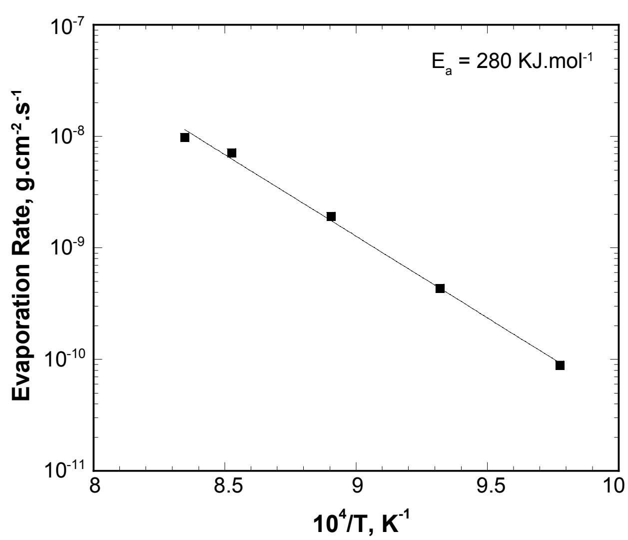

FIGURE 2. The Evaporation Rate of Pure Ag as a Function of Exposure Temperature in a Flowing Air of 1.5 cm.s^{-1}

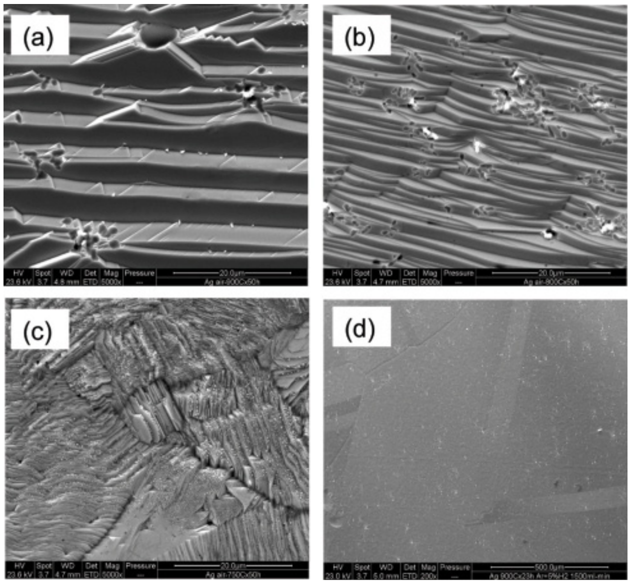

FIGURE 3. Surface morphological features of polycrystalline Ag developed after thermal exposure with a gas flow rate of 1.5 cm.s-1: (a) 900°C, air, 50 hours; (b) 800°C, air, 50 hours; (c) 750°C, air, 50 hours; and (d) 900°C, Ar+5%H2, 20 hours.

decrease the evaporation of Ag. The effects of various alloying elements, such as other noble metals which can form solid solution and surface-active elements which segregate to the alloy surface, on reducing the evaporation rate of Ag is under investigation in the PI's lab. The fundamental study on the evaporation of pure Ag has also helped define the optimal exposure conditions for evaluating the effect of alloying additions on Ag evaporation. The parameters for the exposure experiments in evaluating the Ag evaporation of Ag-based alloys as contact materials have been identified as follows: exposure environment – flowing air; air flow rate – 1.5 cm/s; exposure temperature – 850°C; exposure time – 40 hours. These parameters are being used in the systematic study of the effects of alloying additions on the Ag evaporation.

Conclusions and Future Directions

The following conclusions can be drawn based on this study:

- The evaporation of Ag initially increased linearly with air flow rate and then reached a plateau at a flow rate of about 1.0 cm.s^{-1}; further increase in air flow rate had no effect on the Ag evaporation.
- The exposing atmosphere has no noticeable influence on the Ag evaporation rate, although different surface morphologies developed after thermal exposure.
- The heats of evaporation were very close to the heat of atomization for pure Ag.
- Alloying Ag with other elements, which can increase the bonding energy, might decrease the evaporation of Ag.

The future directions for this project are listed below:

- A number of binary and ternary Ag alloys will be prepared and the evaporation rate of these alloys with various alloying additions will be measured and potential alloying elements which can significantly reduce the Ag evaporation will be identified.
- A series of Ag+ perovskite composites with different particle sizes and different volume ratios of Ag/perovskite will be synthesized and the sintering behavior of these composites will be studied.
- The performance of the contact materials will be evaluated including their interaction with interconnect and cathode materials and their effectiveness on blocking Cr migration from the interconnect alloy to the cathode.

FY 2006 Publications/Presentations

1. "Evaporation and Thermal Etching of Pure Ag at Elevated Temperatures", Z.G. Lu and J.H. Zhu (manuscript to be submitted to J. Electrochem. Soc.).

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